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(21) International Application Number: PCT/EP98/03291 (22) International Filing Date: 2 June 1998 (02.06.98) (30) Priority Data: 970418 4 June 1997 (04.06.97) IE (71) Applicant (for all designated States except US): CHEMICAL TECHNOLOGIES AND KNOW-HOW LIMITED [-/-]; 22 Grenville Street, Saint-Helier, Jersey (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): GUBSER, Andreas [CH/CH]; Thurgauerstrasse 40, CH-8050 Zurich (CH). (74) Agent: SARPI, Maurizio; Studio Ferrario, Via Collina, 36, I-00187 Roma (IT).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PROCESS FOR PRODUCTION OF AROMATIC TRICARBOXYLIC ACIDS		
(57) Abstract <p>The production of aromatic tricarboxylic acids like trimellitic acid, is enhanced by conducting an improved catalytic liquid phase oxidation of a trimethyl substituted aromatic hydrocarbon, as pseudocumene, continuously in at least three stages of reaction in series. The use as promoter of a ketone or an aldehyde at the first stage of reaction and of bromine at the following stages, in combination with the use of oxygen as oxidizing medium, allows to reduce substantially the global consumption of metal catalysts (Co, Mn, Zr, Ce) and to achieve high values of conversion and of selectivity.</p>		

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PROCESS FOR PRODUCTION OF AROMATIC TRICARBOXYLIC ACIDS

BACKGROUND OF THE INVENTION

The process described herein relates to the production of aromatic tricarboxylic acids having only two vicinal carboxylic acid groups and more particularly it pertains to an improved technique for catalytic liquid phase oxidation of a trimethyl substituted aromatic hydrocarbon having only two methyl substituents on vicinal ring carbons, such as pseudocumene to an aromatic tricarboxylic acid having only two carboxylic acid group substituents on vicinal ring carbons and having the third carboxyl group as a substituent on a non-vicinal ring carbon, such as trimellitic acid.

The conversion of trimethyl substituted aromatic hydrocarbons by catalytic liquid phase oxidation in the presence of heavy metal oxidation catalysts and side chain oxidation initiators or promoters to aromatic tricarboxylic acids is described in the technical literature. In general, the uses of different catalytic systems are proposed. All employ heavy metals of the class of those having atomic weight from about 50 to about 200, desirably those in this class which are of variable valence or transition metals, and show a preference for using cobalt, alone or in combination with manganese. These oxidation metal catalysts are usually introduced in a form which is soluble in the hydrocarbon to be oxidized and/or an oxidation solvent medium is which preferably acetic

acid. The catalyst systems are provided by the use in combination with said heavy metals of one promoter or initiator of side chain oxidation, which is typically a compound containing bromine.

5 Any form of bromine supplying ionic bromine in the reaction system, i.e. hydrogen bromide or combined bromine as in organic bromides, can be used. The discovery of the system of catalysis provided by heavy metal oxidation catalysts and bromine for the rapid,
10 high conversion of di-, tri- and other polysubstituted aromatic compounds with air in a liquid system on a once through basis is described in U.S. Patent No. 2,833,816. Later patents teach applications of said unique system of catalysis to various means for
15 exploiting that oxidation method, for the commercial production of benzene tricarboxylic acids. As described in U. S. Patent No 3,920,735, it has been found that zirconium is unique among the Group IV B metals to substantially enhance the activity of the
20 bromine-cobalt or the bromine-cobalt-manganese systems of catalysis.

The use of cerium in association with cobalt or cobalt-manganese as transition metal catalyst is described in US Pat. No 3,491,144 and US Pat. No
25 3,683,016.

In general the aforementioned catalytic liquid phase oxidations using air as a source of molecular oxygen are conducted at 150°C to 250°C and at a pressure adequate to maintain a liquid phase of alkyl
30 substituted aromatic hydrocarbons. Commercial

developments utilizing the foregoing systems of catalysis employ controlled reaction temperature within a narrow range; staged reaction temperatures such as those starting at a low or initiation temperatures, increasing reaction temperature, to obtain maximum oxidation or substantial completion of the oxidation to oxidize small amounts of partial oxidation by-products such as for example methylol benzoic acids, formylbenzoic acid. Staged oxidations have been applied to time staged intermittent batchwise or semicontinuous mode of operation.

It has been found that certain polymethyl substituted aromatic compounds, when oxidized in the foregoing catalytic liquid oxidation systems, appear to produce oxidation by-products which provide undesired autoinhibitions of oxidation. That is, there are formed partial oxidation products which prevent substantial completion of the oxidation of the polymethyl substituted aromatic hydrocarbon feeds to the desired aromatic polycarboxylic acids. This autoinhibition is most pronounced in the oxidation of aromatic compounds having two methyl substituents on vicinal ring carbons, like 1, 2, 4 trimethylbenzene (pseudocumene). In the catalytic liquid phase oxidation of pseudocumene the autoinhibition has the effect of limiting trimellitic acid yields to the range of 65% to 75% mol. The effect of autoinhibition appears to be that of preventing the oxidation of methyl substituted phthalic acids to trimellitic acid and the oxidation of reducible partial oxidation

products such as formyl phthalic acids and methylol phthalic acids to trimellitic acid. Trimellitic acid appears to have an autoinhibiting effect on the oxidation of pseudocumene rather than an auto-oxidative effect. Some free radical mechanisms are believed to adversely affect the oxidation of methyl phthalic acids and the reducible partial oxidation products. The same or a similar autoinhibition occurs in the catalytic liquid phase oxidation of other trimethyl substituted aromatic compounds having only two methyls on vicinal ring carbons.

It has been found that a higher thermal driving force, higher reaction temperature or a selected stage of use of higher reaction temperature in batch operation, effectively results in higher trimellitic acid yields.

However, reaction temperatures above 230°-240°C induce decarboxylation of trimellitic acid to phthalic acids and the ultimate result is a lower rather than a higher trimellitic acid yield.

The preparation of trimellitic acid by oxidation of pseudocumene in the presence of lower alkanolic acid reaction solvents presents a problem of its own. Trimellitic acid is substantially soluble in the reaction solvent media to make recovery of more than about 65% to 70% of trimellitic acid commercially not feasible by the crystallization thereof from the liquid reaction mixture. Thus the lower the oxidation yield of trimellitic acid the lower will be the recovery of the desired product from a crystallization technique.

Trimellitic acid recovery can be increased by removing a substantial portion or all of the acidic reaction solvent. However, when there are also present large amounts of such by-products as benzoic acid (two -COOH groups being lost by decarboxylation), the three phthalic acid isomers, methylphthalic acids, reducible partial oxidation products such as formyl phthalic acids and methylol phthalic acids and the like, there are too many closely related acid impurities in admixture with trimellitic acid to make a commercially feasible recovery of it in a suitably pure form. A recovery system wherein the total liquid reaction mixture is distilled, trimellitic acid is dehydrated to its intramolecular anhydride and this anhydride is distilled off, recovered and becomes a feasible commercially recovery system, provided a high yield of trimellitic acid and a lower yield of methylphthalic acids and reducible partial oxidation products is obtainable.

It has been discovered, and described in the literature, that the prior oxidation problems which came from the autoinhibitions during pseudocumene oxidation in a catalytic liquid phase system was provided, in general, by having too active a catalyst system in the beginning and during about 2/3 of the oxidation and a system not sufficiently active in the last of the oxidations. By oxidation rate studies applied to the oxidation of the second and the third methyl groups it has been shown how the catalytic liquid phase oxidation of pseudocumene could be

conducted in order to achieve higher yields of conversion.

The oxidation rate studies have shown that the yields of liquid phase oxidations of trimethyl substituted aromatic hydrocarbons, such as pseudocumene, can be improved using, during the initial stage of the oxidation of pseudocumene, a combination of side-chain initiator bromine with heavy metal catalysts having the oxidation potential at least equal to that of cobalt and manganese.

In the following stages of reaction, the temperature is increased while additional catalyst consisting of manganese, alone or in association with zirconium and/or cerium, is added with additional bromine promoter.

The staged batch mode of operation of the reaction, as described in U.S. Pat. No 3,920,715 and in other patents, although providing a more efficient system of reaction compared with the previous status of the technology of oxidation of trimethyl substituted aromatic hydrocarbons, still presents several disadvantages.

The consumption of metal catalysts substantially contributes to the cost of production of trimellitic anhydride.

Recycle of catalyst is mentioned in the literature, but requires rather complex and expensive procedures for freeing the metals from the contaminants.

Furthermore, batch oxidations have disadvantages

because the concentration of the hydrocarbon to be oxidized is high at the start of the reaction and its rate of oxidation is difficult to control. This leads to a low concentration of dissolved oxygen and to an increased amount of radical reaction producing high boiling point by-products which reduce the yield. Thermally induced destruction of methyl groups occurs, leading to the formation of xylenes, which become oxidized to dicarboxylic acids, contributing to yield losses.

Finally the batch mode of operation requires additional operating costs and presents higher safety hazards due to the risk of forming explosive mixtures particularly at the transient conditions of the reaction (i.e.: start and end of the batch).

The abovementioned disadvantages are to a large extent reduced by the improved process object of the present invention.

DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide an improved process for production of tricarboxylic acids having only two carboxylic acid group substituents on vicinal ring carbons, such as trimellitic acid, by means of catalytic liquid phase oxidation of trimethyl substituted aromatic hydrocarbons having only two methyl substituents on vicinal ring carbons, such as pseudocumene.

As described in the background, the liquid phase oxidation reaction, as applied to pseudocumene, is very difficult and has been industrially practiced as a

batch process because the reaction product, trimellitic acid, is a poison for the catalyst.

The present invention provides an improved method for a continuous liquid phase oxidation of pseudocumene with an oxygen containing gas, in the presence of suitable oxidation catalysts.

More particularly, it is an object of the present invention to provide an improved method for effecting the mentioned oxidation process to produce trimellitic acid to be converted to trimellitic anhydride, with improved selectivity and yield.

It is a related object of the present invention to provide an improved method for effecting the aforesaid oxidation process continuously.

It is a further object of the present invention to provide an improved method for effecting the aforesaid oxidation process using reduced amounts of metal catalysts.

These objects are achieved by an improved method of a staged continuous liquid phase oxidation of a trimethyl aromatic feedstock, such as pseudocumene, to produce an aromatic tricarboxylic acid such as trimellitic acid, comprising:

- a) providing at least three stages of reaction in series consisting of one initial reactor, one or more than one intermediate reactor, one final reactor
- b) introducing into the initial reactor an oxygen containing gas, the aromatic feedstock, a solvent, preferably acetic acid, and a primary catalyst provided

by transition or variable valence metals, such as cobalt and/or manganese. The catalysis is promoted by the use of a ketone such as methylethylketone or an aldehyde such as, and preferably, acetaldehyde.

5 The temperature at the initial reactor is from 90°C to 140°C, preferably from 120°C to 130°C.

c) introducing into the intermediate reactor(s) an oxygen containing gas, the effluent from the first reactor and a secondary catalyst consisting of heavy
10 metal oxidation catalysts such as cerium and zirconium. In the intermediate reactor(s) the catalysts are provided by the addition of bromine in the form of organic or inorganic compounds, such as hydrogen bromide.

15 The temperature at the intermediate reactor(s) is from 130° to 190°C, preferably from 160° to 180°C.

d) introducing into the final reactor an oxygen containing gas, the effluent from the intermediate reactor(s) and a stream of mother liquor containing the
20 catalyst and recovered from the product separation section, reactivated by the addition of bromine. The temperature at the final reactor is from 170°C to 220°C preferably from 180° to 210°C.

e) operating the reaction system at a pressure not
25 inferior to the minimum pressure necessary to maintain the liquid phase of the solvent.

f) using, as oxidizing medium, oxygen being dissolved in a recycling stream of reaction gas effluents, mostly consisting of carbon dioxide, carbon monoxide, water,
30 solvent and organic vapors.

g) adjusting the oxygen content in each stage of the reaction in order to assure an adequate oxidation rate, assuring at same time that, for safety purposes, the oxygen concentration in the exhaust gas does not exceed 8% by volume.

The use of a ketone, such as methylethylketone, or of an aldehyde, such as acetaldehyde as promoter of the catalysis provided by transition or variable valence metals in liquid phase oxidations for the preparation of benzene carboxylic acids, has been described in US Pat. No 2,245,528 and practiced in the industry for the production of terephthalic acid and isophthalic acid.

However, such an aldehyde or ketone promoted catalysis was found not suitable in the oxidation of trimethylbenzene being only capable of converting the trimethylbenzene to its benzene mono- and dicarboxylic derivatives.

It has now been found that the use of a ketone or of an aldehyde, preferably acetaldehyde, in the initial stage of a reaction system comprising at least 3 stages of reaction in series, eliminates the risk of autoinhibition, reduces the amount of metal catalysts and of bromine activator and allows to recycle to the final stage of reaction a fraction of the mother liquor, containing metal catalyst, recovered after crystallization and filtration of the reactor effluent, allowing a substantial reduction of the global consumption of metal catalysts.

The performances of this novel process of catalytic oxidation of pseudocumene to trimellitic acid

are enhanced by the use of oxygen as the oxidizing agent.

Optimum overall performances can be achieved by optimising, at each stage of reaction, the major operating parameters such as the temperature, the partial pressure of oxygen in the oxidizing medium, the concentration of a primary and secondary metal catalysts, the concentration of the promoter (aldehyde or ketone in the initial stage, bromine in the intermediate and final stages), the amount of mother liquor containing catalyst being recycled to the final stage of reaction.

The embodiments of the process object of the present invention can be illustrated by the following examples:

EXAMPLE (STANDARD)

STANDARD experiments were carried out in three 5 liter fully equipped autoclaves connected in series.

Oxygen, dissolved in a recycling off gas stream, was used as the oxidizing agent.

A feedstock mixture was continuously introduced in the first autoclave consisting of 480 gr of pseudocumene, 960 gr of acetic acid containing 4% of water, 50 g of acetaldehyde and with a primary catalyst consisting of 360 mg of cobalt, supplied in the form of cobalt acetate, and of 240 mg manganese, supplied in the form of manganese acetate.

The mixture was oxidized at a temperature of about 125°C. The oxidizing medium was oxygen with 16% vol concentration in a gaseous stream consisting of carbon

dioxide, carbon monoxide, water and acetic acid vapours plus minor amounts of inerts.

The effluent from the first autoclave was continuously transferred to the intermediate autoclave where an additional stream of catalytic component (secondary catalyst) was added, consisting of 5 mg of zirconium, supplied in the form of zirconium octanoate, of 20 mg of cerium, supplied in the form of cerium chloride, and of 400 mg of bromine supplied in the form of hydrogen bromide.

In the intermediate autoclave the oxidation was continued at a temperature of about 170°C. The oxidizing medium was oxygen with 19% by vol. concentration in the gaseous stream of the abovementioned composition.

The effluent from the intermediate autoclave was continuously transferred to the third autoclave where an additional stream was added consisting of recycling mother liquor containing about 150 mg of metals (Co-Mn-Ce-Zr) catalysts, added with 250 mg of fresh hydrogen bromide.

In the third autoclave the oxidation was completed at a temperature of about 195°C.

The oxidizing medium was oxygen with 21% by vol. concentration in a gaseous stream of the abovementioned composition.

The overall performances of the reaction resulted as follows:

yield in trimellitic acid:	92,8% mol
yield in by-product:	3,4% mol

yield in CO+CO₂ : 3,8% mol

Following crystallization, a crude solid stream of trimellitic acid was separated by filtration and a fraction of mother liquor, containing about 150 mg of metals (Co, Mn, Ce, Zr) was recycled to the third autoclave.

The pressure in the reaction system was about 24 Bar.

COMPARATIVE EXAMPLE A

The STANDARD experiment was repeated, replacing the acetaldehyde fed to the first autoclave with 250 mg of bromine and operating the first autoclave at a temperature of 160°C instead of 125°C.

The performance of the reaction resulted as follows:

yield in trimellitic acid :	82,7% mol
yield in by-products:	12,2% mol
yield in CO+CO ₂ :	5,1% mol

COMPARATIVE EXAMPLE B

The experiment described in COMPARATIVE EXAMPLE A was repeated without recycling mother liquor containing metal catalysts to the third autoclave.

The performances of the reaction resulted as follows:

trimellitic acid product yield:	84,2% mol
by-product yield:	10,9% mol
CO+CO ₂ yield:	4,9% mol

COMPARATIVE EXAMPLE C

The experiment described in COMPARATIVE EXAMPLE B was repeated doubling the amount of metal catalyst and of bromine fed to each reactor.

5 The performances of the reaction resulted as follows:

trimellitic acid product yield:	89,9% mol
by-product yield:	5,2% mol
CO+CO ₂ yield:	4,9% mol

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COMPARATIVE EXAMPLE D

The STANDARD experiment was repeated in identical conditions using air instead of oxygen.

15 The performances of the reaction resulted as follows:

trimellitic acid product yield:	90,2% mol
by-product yield:	4,9% mol
CO+CO ₂ yield:	4,9% mol

CLAIMS

1. A process for the production of aromatic tricarboxylic acids like trimellitic acid, by continuous liquid phase oxidation of a trimethyl aromatic feedstock like pseudocumene, comprising:

- 5 a) providing at least three stages of reaction in series consisting of one initial reactor, one or more than one intermediate reactor, one final reactor;
- b) introducing into the initial reactor an oxygen
10 containing gas, the aromatic feedstock, a solvent, and a primary catalyst provided by transition or variable valence metals, such as cobalt and/or manganese; the catalysis being promoted by the use of a ketone such as methylethylketone or an
15 aldehyde; the temperature at the initial reactor being between 90°C and 140°C;
- c) introducing into the intermediate reactor(s) an oxygen containing gas, the effluent from the first reactor and a secondary catalyst consisting of
20 heavy metal oxidation catalysts such as cerium and zirconium; in the intermediate reactor(s) the catalysts being provided by the addition of bromine in the form of organic or inorganic compounds, such as hydrogen bromide; the
25 temperature at the intermediate reactor(s) ranging between 130° to 190°C;
- d) introducing into the final reactor an oxygen containing gas, the effluent from the intermediate

reactor(s) and a stream of mother liquor containing the catalyst recovered from the product separation section and reactivated by the addition of bromine; the temperature at the final reactor being from 170°C to 220°C;

e) operating the reaction system at a pressure not lower than the minimum pressure necessary to maintain the solvent at the liquid phase;

f) using as oxidizing medium oxygen being dissolved in a recycling stream of reaction gas effluents, mostly consisting of carbon dioxide, carbon monoxide, water, solvent and organic vapours;

g) adjusting the oxygen content in each stage of reaction in order to assure an adequate oxidation rate, assuring at same time that for safety purposes, the oxygen concentration in the exhaust gas does not exceed 8% by volume.

2. A process for the production of aromatic tricarboxylic acids like trimellitic acid, by continuous liquid phase oxidation of a trimethyl aromatic feedstock like pseudocumene according to claim 1, characterised by the fact that the temperature at the initial reactor is between 120°C and 130°C.

3. A process for the production of aromatic tricarboxylic acids like trimellitic acid, by continuous liquid phase oxidation of a trimethyl aromatic feedstock like pseudocumene according to claims 1, characterised by the fact that at the initial

reactor the solvent is acetic acid and the catalysis is promoted by acetaldehyde.

4. A process for the production of aromatic tricarboxylic acids like trimellitic acid by continuous liquid phase oxidation of a trimethyl aromatic feedstock like pseudocumene according to claim 1, characterised by the fact that the temperature at the intermediate reactor is between 160° and 180°C.

5. A process for the production of aromatic tricarboxylic acids like trimellitic acid, by continuous liquid phase oxidation of a trimethyl aromatic feedstock like pseudocumene according to claim 1, characterised by the fact that the temperature at the final reactor is between 180° and 210°C.

6. A process according to claims 1 and 3, characterised by the fact that the ketone or aldehyde promoter fed to the first reactor varies from 5% to 20% wt, relatively to trimethylbenzene.

7. A process according to claim 6, characterised by the fact that the ketone or aldehyde promoter, fed to the first reactor varies from 8% to 12%, wt relatively to trimethylbenzene.

8. A process according to claim 1, 3 and 6, characterised by the fact that the concentration of metal component, cobalt and manganese in the first

reactor (primary catalyst) varies between 0,1% and 0,3% by weight, relatively to the trimethylbenzene feed.

9. A process according to claim 8, characterised by the fact that the concentration of metal component, cobalt and manganese, in the first reactor (primary catalyst) varies between 0.1% and 0.2% wt with respect to the trimethylbenzene feed.

10. A process according to claim 8, characterised by the fact that the concentration of manganese in the primary catalyst is between 25% to 50% wt, referred to the total weight of primary catalyst.

11. A process according to claim 10 where the concentration of manganese in the primary catalyst is from 35% to 45% wt, referred to the total weight of primary catalyst.

12. A process according to claim 1, characterised by the fact that the concentration of cerium plus zirconium metal components fed to the intermediate reactor(s) (secondary catalyst) varies between 0,002% and 0,01% wt with respect to the trimethylbenzene feed.

13. A process according to claim 12, where the concentration of cerium plus zirconium metal component fed to the intermediate reactor(s) (secondary catalyst) varies between from 0,004% to 0,006% by weight, with respect to the trimethylbenzene feed.

14. A process according to claim 1, characterised by the fact that the concentration of zirconium in the secondary catalyst is between 10% to 40%, referred to
5 the total amount of secondary catalyst.

15. A process according to claim 14, characterised by the fact that the concentration of zirconium in the secondary catalyst is from 15% to 25%
10 wt of the total amount of secondary catalyst.

16. A process according to claims 1 and 12, characterised by the fact that the concentration of bromine fed to the intermediate reactor(s) varies
15 between 0,06% and 0,15%, relatively to the trimethylbenzene feed.

17. A process according to claim 16, characterised by the fact that the concentration of
20 bromine fed to the intermediate reactor(s) varies between 0,08% to 0,12% wt, relative to the trimethylbenzene feed.

18. A process as defined in claim 1,
25 characterised by the fact that a fraction of the mother liquor stream recovered after the separation of trimellitic acid, is recycled to the final reactor and contains from 10% to 40% of the total fresh metal catalysts (Cobalt, Manganese, Zirconium, Cerium) fed to
30 the reaction system.

19. A process as defined in claim 18 characterised by the fact that a fraction of the mother liquor stream recovered after the separation of trimellitic acid, is recycled to the final reactor and contains from 20% to 30% wt of the total fresh metal catalysts (Cobalt, Manganese, Zirconium, Cerium) fed to the reaction system.

20. A process according to claim 1, characterised by the fact that the concentration of bromine fed to the final reactor ranges between 0,02% to 0,1% wt, with respect to the trimethyl benzene feed.

21. A process according to claim 20 characterised by the fact that the concentration of bromine fed to the final reactor varies between 0,04 to 0,08% wt, with respect to the trimethyl benzene feed.

22. A process according to claims 1 to 21, characterised by the fact that the product is trimellitic anhydride.

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INTERNATIONAL SEARCH REPORT

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PCT/EP 98/03291

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C51/265 C07C63/307

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US 3 683 016 A (DARIN JOHN K ET AL) 8 August 1972 cited in the application see column 2, line 44 - column 3, line 64 see example 3 see claims ---	1
A	US 3 920 735 A (WAMPFLER GENE L ET AL) 18 November 1975 cited in the application see column 1, line 8 - line 32 see column 2, line 65 - column 3, line 3 see column 7, line 26 - line 34 see table II see claims --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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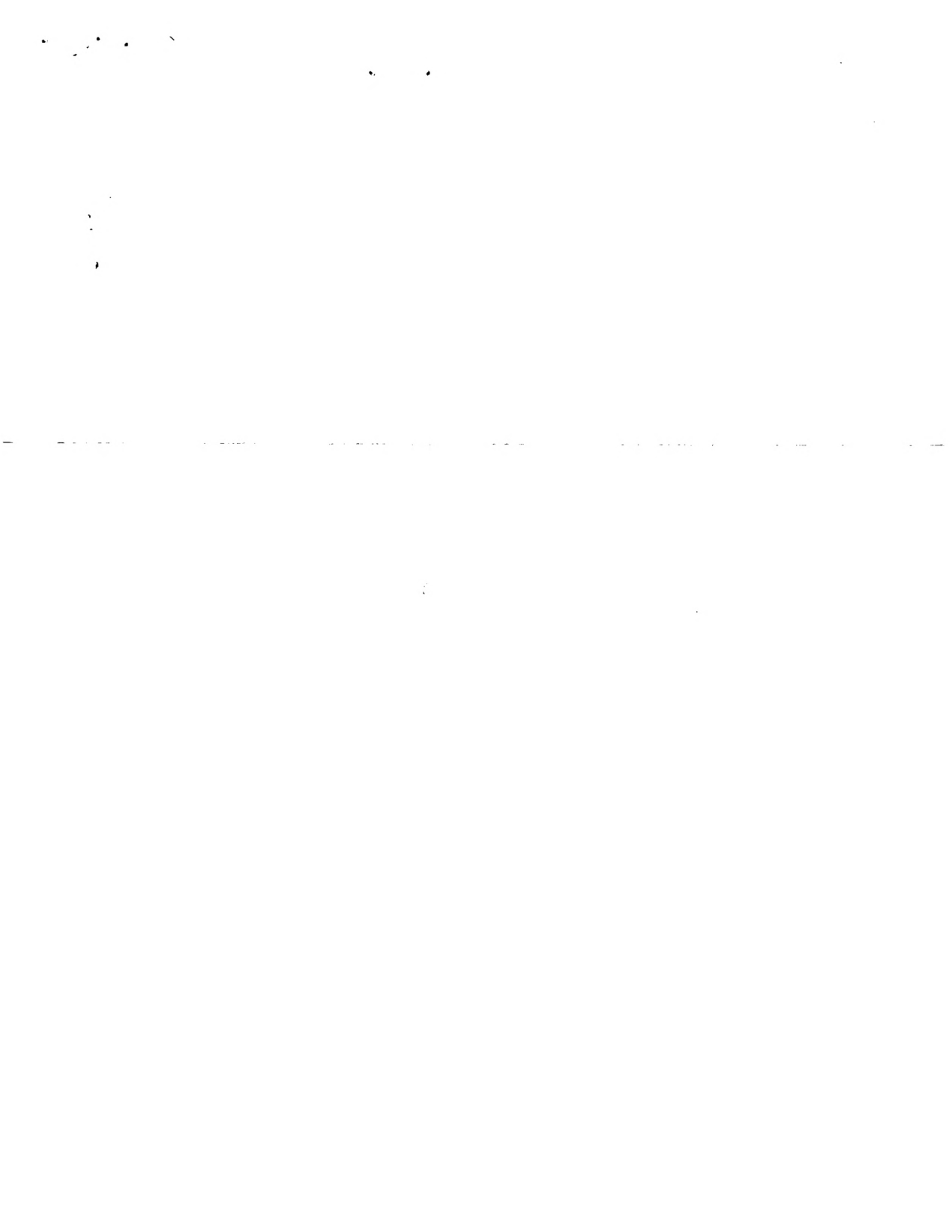
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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